

Differences in the Concentrations of Priority Pollutant Metals in Seawater Samples from Puget Sound and the Strait of Georgia

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Introduction

The Washington State Department of Ecology (WDOE) requires industrial discharges to determine the concentrations of relevant metals in receiving water as part of the process for renewing wastewater discharge permits. These concentrations of metals in receiving water are considered in establishing environmental protective discharge limits. The study reported here was conducted to determine the concentrations of 13 U.S. EPA priority pollutant metals in surface seawater of three regions of Puget Sound. The seawater samples were collected and analyzed using new “clean metals” methods EPA has drafted for measuring the concentrations of ambient metals in seawater with detection limits in the range of 0.0002 to 0.3 µg/L. The results reported here are the only known data on regional concentrations of several metals in Puget Sound.

Methods

The three regions included Cherry Point, northwest of Bellingham in the Strait of Georgia only 16 km from Canadian waters; March Point near Anacortes, at the eastern edge of the San Juan Islands; and Commencement Bay, the industrial harbor in Tacoma. At each region a grid of 10 stations was sampled once in the summer of 1997. The grid covered an area approximately 3 by 6 km. The sampling stations were selected to minimize the influence from local point sources, such as outfalls, rivers, and marinas. The location of the stations was determined by a global positioning system (GPS) and the coordinates are given in Tables 1–3.

Table1. Results for conventional water properties - Cherry Point stations, sample date: July 16, 1997

Station #	North Latitude	West Longitude	Temp. (°C)	pH	TSS (mg/L)	Salinity (ppt)
CP 1	48° 52.3479 N	122° 47.357 W	16.0	8.18	0.800	18.6
CP 2	48° 52.2295 N	122° 46.7617 W	16.5	8.13	1.07	18.8
CP 3	48° 51.1480 N	122° 47.9152 W	17.0	8.14	1.20	18.3
CP 4	48° 51.0656 N	122° 46.4797 W	16.5	8.08	0.933	19.4
CP 5	48° 49.9481 N	122° 45.9158 W	16.1	8.03	1.07	18.0
CP 6	48° 49.5052 N	122° 46.7361 W	17.3	8.00	2.13	17.3
CP 7	48° 49.3868 N	122° 44.6598 W	17.2	7.99	0.933	18.2
CP 8	48° 48.4752 N	122° 45.6082 W	16.7	8.18	0.400	20.4
CP 9	48° 48.9130 N	122° 43.7114 W	17.8	8.15	1.60	19.5
CP 10	48° 48.1353 N	122° 43.7883 W	16.7	8.07	1.07	19.1
	mean		16.8	8.10	1.12	18.8
	standard deviation		0.555	0.0714	0.467	0.883

Table 2. Results for conventional water properties - March Point stations, sample date: June 30, 1997

Station No.	North Latitude	West Longitude	Temp. (°C)	pH	TSS (mg/L)	Salinity (ppt)
MP 1	48° 32.5880 N	122° 33.8639 W	13.6	7.94	2.00	25.6
MP 2	48° 31.9082 N	122° 33.8349 W	13.1	7.96	1.60	27.4
MP 3	48° 31.6507 N	122° 36.5017 W	11.5	7.87	1.87	28.8
MP 4	48° 31.6130 N	122° 35.4594 W	11.6	7.88	2.27	28.3
MP 5	48° 31.5117 N	122° 34.7710 W	12.2	7.88	2.13	28.4
MP 6	48° 31.4859 N	122° 33.5712 W	13.8	7.96	2.27	27.4
MP 7	48° 31.0739 N	122° 35.0702 W	12.4	7.93	2.80	28.3
MP 8	48° 31.1254 N	122° 34.2370 W	12.0	7.90	3.73	28.6
MP 9	48° 30.9967 N	122° 33.5326 W	13.8	7.96	2.00	27.2
MP 10	48° 30.6619 N	122° 32.9889 W	14.5	8.02	1.73	27.6
mean			12.9	7.93	2.24	27.8
standard deviation			1.05	0.0476	0.621	0.945

Table 3. Results for conventional water properties - Commencement Bay stations, sample date: July 11, 1997

Station No.	North Latitude	West Longitude	Temp. (°C)	pH	TSS (mg/L)	Salinity (ppt)
CB1	47° 17.4981 N	122° 26.2301 W	13.5	7.78	4.13	27.0
CB2	47° 17.4054 N	122° 25.4101 W	15.7	7.79	3.07	25.3
CB3	47° 17.0965 N	122° 26.8007 W	13.2	7.80	7.33	26.5
CB4	47° 16.9523 N	122° 26.0544 W	13.8	7.79	2.40	27.4
CB5	47° 17.2406 N	122° 24.8263 W	16.5	7.78	2.53	22.2
CB6	47° 16.9574 N	122° 25.2854 W	14.9	7.79	2.53	26.0
CB7	47° 16.7257 N	122° 25.6520 W	13.5	7.76	3.20	27.6
CB8	47° 16.5094 N	122° 26.6760 W	13.6	7.75	3.87	27.1
CB9	47° 16.3703 N	122° 26.0865 W	12.8	7.78	16.0	27.9
CB10	47° 16.0678 N	122° 26.4984 W	14.3	7.75	6.00	27.3
mean			14.2	7.78	5.11	26.4
standard deviation			1.18	0.0177	4.15	1.68

The sampling procedures were from the EPA Method 1669: Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels (EPA 1996c). The sampling procedures in Method 1669 are designed to provide reliable results for the detection limits required in the proposed study. Water samples were collected from 1-m depth below the surface with an all-plastic pumping and filter system that minimized contamination or loss of metals from sampling equipment or airborne contamination. Field equipment blanks were used to evaluate contamination from sampling and storage of water samples.

The pumping system was acid-cleaned in the laboratory then sealed in clean polyethylene bags following Method 1669. In the field, the intake end of the sampling tube was held underwater at a depth of 1 m with an acid-cleaned Teflon weight. Before water samples were taken, the tubing and filter were flushed with five volumes of site water. The dissolved sample was collected, then the filter unit removed, and the total recoverable sample collected. Samples were taken for water quality parameters, including pH, salinity, and total suspended solids (TSS). Temperature was determined on site using an electronic thermometer that was hung in the surface water (15-cm depth). The electronic thermometer was compared with a National Institute of Standards and Technology certified mercury thermometer, which agreed within 0.1°C.

Water samples for metals were collected in Teflon bottles that were acid-cleaned and double-bagged, following Method 1669. After the water samples were collected, they were transported at 4°C to the Marine Science Lab (MSL), where the samples were acidified to pH 2 with high purity nitric acid in a class 100 clean room. One trip blank (for each of the three regions) of metal-free reagent water acidified to pH 2 was taken to the field and returned with the field samples without being opened in the field. One equipment blank was processed at each of the three regions by pumping unacidified reagent water through the field pumping system with and without a filter. This produced a total recoverable and a dissolved field equipment blank. A field duplicate sample for both total recoverable and dissolved metals, as well as water for matrix spikes, was collected at one station at each region.

Analytical Procedures

The analytical procedures were selected to provide detection limits generally a factor of five below the WDOE required detection limits (Table 4). Consideration was also given to the cost of various methods and the expected ambient concentrations of metals in Puget Sound. For the detection limits proposed in Table 4, the ambient concentrations for eight metals (arsenic, cadmium, chromium, copper, lead, mercury, nickel, and zinc) in Puget Sound are usually above the proposed detection limits. The other five metals (antimony, beryllium, selenium, silver, and thallium) are typically present in Puget Sound and other coastal seawater at concentrations of 0.001 to 0.04 µg/L. The cost of detecting these metals in seawater at or below ambient concentrations would be very high, and therefore, we have recommended a detection limit that is well below the WDOE requirement but that may not detect these metals in Puget Sound. The analytical methods that were used are listed in Table 4. These methods have been developed recently by the EPA. Battelle had a significant role in the validation of these methods.

The sampling, storage, and analysis of the conventional water quality parameters followed the analytical procedures in EPA (1983) for pH (Method 150.1) and TSS (Method 160.2). Salinity samples were analyzed by the University of Washington Marine Chemistry Laboratory, with results traceable to a certified salinity standard. A standard salinity sample (Lot P83 11/10 1978) from the Institute of Oceanographic Sciences, Surrey, England, was analyzed three times during the analysis of the field samples. The standard is certified to contain a salinity of 35.003‰. The results from the university laboratory were in excellent agreement ranging from 34.984 to 35.005‰. The surface water temperature was measured in the field using a thermometer that was calibrated against a thermometer certified by the National Institute of Standards and Technology.

Table 4. Required and obtained detection limits and analytical methods for metals in marine water.

POLLUTANT PARAMETER	DETECTION LIMIT REQUIRED ⁽¹⁾ (mg/L)	DETECTION LIMIT OBTAINED ⁽²⁾ (mg/L)	ANALYTICAL METHOD
Antimony (An)	3	0.009	EPA 1640
Arsenic (As)	1.0	0.14	EPA 1640
Beryllium (Be)	1.0	0.0003	EPA 1640
Cadmium (Cd)	0.1	0.006	EPA 1640
Chromium (Cr)	1.0	0.06	EPA 1640
Copper (Cu)	1.0	0.1	EPA 1640
Lead (Pb)	1.0	0.006	EPA 1640
Mercury (Hg)	0.2	0.0002	EPA 1631
Nickel (Ni)	1.0	0.08	EPA 1640
Selenium (Se)	2.0	0.02	EPA 1640
Silver (Ag)	0.2	0.01	EPA 1637
Thallium (Tl)	1.0	0.0006	EPA 1640
Zinc (Zn)	4.0	0.34	EPA 1640

(1) Detection limits required by WDOE.

(2) Detection limits obtained by Battelle based on 3.14 times the standard deviation for the mean of seven water samples from Cherry Point.

Quality Control Procedures

Quality control (QC) procedures provide the means of controlling and reporting the precision and bias (accuracy) of the results. The EPA methods that were followed for sampling and chemical analysis include established procedures that minimize errors. The QC results were used to assess the precision and accuracy of the data.

Three sets of field duplicates were collected, one at each region. The results from the duplicates are used to estimate precision. Three sets of matrix spikes were analyzed and the results used to estimate accuracy. Also, estimates of precision and accuracy were calculated from the analysis of triplicates of certified reference coastal seawater CASS-3 obtained from the National Research Council of Canada. Three trip blanks are used to evaluate contamination from bottles, acid, transportation, and storage. Three field equipment blanks are used to evaluate contamination from field sampling. Reagent or procedural blanks are used to evaluate contamination from the laboratory procedures including reagents, and plastic ware.

Results

Quality Control For Sample Contamination

The sources of contamination for metals were evaluated by analyzing field equipment blanks, trip blanks, and reagent blanks. Generally, contamination was very low compared to the concentration of metals in the field samples. Silver was the only metal that was usually not detected because of the reagent blank. For some dissolved samples, the reagent blank prevented the detection of chromium, zinc, and lead.

Two equipment blanks, one dissolved and one total, were processed from each of the three field sampling regions. For most of the metals there is no difference between the dissolved (filtered) and total (unfiltered) blanks, indicating that the filtering process did not cause significant contamination. For several metals (cadmium, chromium, copper, lead, and zinc) the dissolved blanks were slightly higher than the total blank for two of the three regions. The mean of the six equipment blanks was subtracted from all the field samples to blank-correct the field data for contamination that may have occurred during sampling, transport, storage, and analysis.

Three trip blanks were analyzed to evaluate contamination from transport and storage of the water samples. The trip blanks were reagent water that was acidified in the laboratory before the field sampling trips. The trip blanks were transported to the field, but never opened, then stored and analyzed with the field samples. The results of the trip blanks are very similar to those of the equipment blanks, which indicates the sampling process did not cause significant contamination.

Three reagent blanks were analyzed along with the field samples to estimate contamination caused by the analytical procedure. The mean of the three reagent blanks is similar to the equipment blanks and trip blanks, indicating that the reagent blanks are the most significant source of contamination. The means of the reagent blanks were subtracted from the results for the certified reference seawater (CASS-3) results.

Method Detection Limits

The method detection limits were determined for this study using the results for dissolved metals for seven stations (Cherry Point, CP-3 to CP-9). These Cherry Point results were relatively uniform, indicating that the water in that area was well mixed. The standard deviation of the mean for the seven stations was multiplied by 3.14 (Students t-value for 99% confidence level). The detection limits listed in Table 5 are equal to or well below those required by the WDOE-approved work plan. For silver and zinc, the mean blank is greater than the detection limit. Reduction of the blank for these two metals is needed to improve the analytical method. Several different lots of reagents were tested, but the reagent blank was not significantly improved.

Accuracy and Precision of Results for Metals

The accuracy of the results for metals is evaluated with both a certified reference material and matrix spikes. The reference materials used include CASS-3, a coastal seawater that is certified for seven metals, and 1641c certified for Hg. The results for the reference materials are shown in Table 6. The results were corrected for reagent blanks to remove that bias from our results. Our results were usually within the QC plan acceptance range of $\pm 20\%$ of the certified value for mercury, nickel, copper, cadmium, and lead. Several metals were outside the acceptance range either due to contamination or low recovery. Some of the chromium, lead, and zinc results were high, probably due to variability of our reagent blank for those three metals. Our reagent blank is relatively high and variable compared with the very low concentration in the reference material. Our results for arsenic averaged 20% lower than the certified value. Our results for selenium are near the reference value or below our detection limit. CASS-3 is not certified for selenium but a reference value is provided. The reference material is not certified for silver, beryllium, mercury, antimony, and thallium.

Matrix spikes and matrix spike duplicates were conducted on both a dissolved and total sample from each of the three field regions. The goal for matrix spike recovery was 80% to 120% and the goal for the relative percent difference (RPD) between duplicate spikes was 20%.

The matrix spikes recoveries for As, Cd, Cr, Cu, Hg, Ni, Pb, and Tl were usually in the range of 80% to 98%. Of the eight metals, the As recovery was often near 80%, which is consistent with the similar low recovery for As in CASS-3. The recoveries of Se and Sb are often in the 60% to 80% range. These two elements are present as anions in seawater, like As. The recovery of Ag was sometimes very low. However, the Ag recovery had no affect on the field results, which were below the detection limit and below the reagent blank. The matrix spike recoveries for Be were often near 80% and for Zn were near 50%. The low and inconsistent Zn recoveries may be due to the low concentration spiking. The results for Zn in CASS-3 were not low, which brings the significance of the Zn matrix spike recoveries into question.

The precision as determined from field duplicates and matrix spike duplicates is very good. Most of the duplicates agree within 10% RPD. The RPDs tend to increase when the concentrations of metals approach the detection limit, such as for silver, beryllium and selenium. The RPDs for the matrix spikes are lower, because the concentrations of metals are generally well above the detection limits.

Table 5. Method Detection Limit (MDL) determination

			(concentration in µg/L, not blank corrected)						
MDL Verification:			Ag	Hg	Be 9	Cr 52	Ni 60	Cu 63	Zn 66
MSL Code	Station ID	Type	GFAA	CVAA	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
1114WSPA*189	CP4	DISS	0.016	0.000390	0.00000	0.130	0.405	0.608	1.57
1114WSPA*190	CP5	DISS	0.011	0.000360	0.00000	0.147	0.377	0.628	1.39
1114WSPA*191	CP6	DISS	0.013	0.000239	0.00029	0.122	0.403	0.637	1.60
1114WSPA*192	CP7	DISS	0.008	0.000270	0.00000	0.124	0.408	0.606	1.34
1114WSPA*193	CP8	DISS	0.008	0.000235	0.00000	0.156	0.363	0.525	1.37
1114WSPA*194	CP9	DISS	0.008	0.000288	0.00000	0.156	0.365	0.564	1.56
1114WSPA*195	CP10	DISS	0.008	0.000374	0.00000	0.176	0.432	0.607	1.43
Standard			0.0032	0.0000654	0.000109	0.0200	0.0256	0.0390	0.107
Deviation:			0						
Mean:			0.0103	0.000308	0.000041	0.144	0.393	0.597	1.46
					0				
MDL (StDev x 3.14):			0.010	0.000205	0.000341	0.0627	0.0803	0.122	0.336

			Continued-(concentration in µg/L, not blank corrected)					
			As 75	Se 77	Cd 112	Sb 121	Tl 205	Pb 207
MSL Code	Station ID	Type	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
1114WSPA*189	CP4	DISS	0.448	0.0088	0.0463	0.0673	0.00821	0.0124
1114WSPA*190	CP5	DISS	0.424	0.0197	0.0488	0.0638	0.00840	0.00811
1114WSPA*191	CP6	DISS	0.418	0.0000	0.0443	0.0639	0.00824	0.00727
1114WSPA*192	CP7	DISS	0.441	0.0068	0.0431	0.0630	0.00801	0.00759
1114WSPA*193	CP8	DISS	0.543	0.0197	0.0471	0.0615	0.00846	0.00656
1114WSPA*194	CP9	DISS	0.419	0.0081	0.0467	0.0605	0.00797	0.00725
1114WSPA*195	CP10	DISS	0.472	0.0155	0.0468	0.0584	0.00811	0.00784
Standard			0.0446	0.00733	0.00189	0.00284	0.000187	0.00195
Deviation:								
Mean:			0.452	0.0112	0.0461	0.0626	0.00820	0.00815
MDL (StDev x 3.14):			0.140	0.0230	0.00594	0.00891	0.000588	0.00612

Table 6. Results for analysis of certified reference waters.

			W.S.P.A. Quality control results (concentration in µg/L, blank corrected)						
MSL Code	Station ID	Type	Ag	Hg	Be 9	Cr 52	Ni 60	Cu 63	Zn 66
			GFAA	CVAA	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
Standard Reference Material									
1641c			NA	1510	NA	NA	NA	NA	NA
1641c			NA	1480	NA	NA	NA	NA	NA
1641c			NA	1440	NA	NA	NA	NA	NA
	certified			1470					
	value								
	range			±40					
	percent		NA	3%	NA	NA	NA	NA	NA
	difference								
			NA	1%	NA	NA	NA	NA	NA
			NA	2%	NA	NA	NA	NA	NA
cass3 r1			0.010	NA	0.000341	0.180	0.388	0.573	2.88
					U				
cass3 r2			0.014	NA	0.000341	0.0994	0.360	0.518	1.27
					U				
cass3 r3			0.008	NA	0.000341	0.0903	0.347	0.513	1.68
					U				
cass3 rerun				NA	0.000341	0.220	0.367	0.559	1.88
					U				
	certified		NC	NC	NC	0.092	0.386	0.517	1.24
	value								
	range					±0.006	±0.062	±0.062	±0.25
	percent		NA	NA	NA	95%	1%	11%	132%
	difference								
			NA	NA	NA	8%	7%	0%	2%
			NA	NA	NA	2%	10%	1%	36%
			NA	NA	NA	139%	5%	8%	52%
Mean reagent blank (used to correct CASS)			0.010	0.000063	0.00055	0.0423	0.0131	0.0283	0.463

Table 6 (Continued). Results for analysis of certified reference waters.

			W.S.P.A. Quality control results continued (concentration in µg/L, blank corrected)					
MSL Code	Station ID	Type	As 75 ICP- MS	Se 77 ICP-MS	Cd 112 ICP-MS	Sb 121 ICP-MS	Tl 205 ICP-MS	Pb 207 ICP-MS
Standard Reference Material								
1641c			NA	NA	NA	NA	NA	NA
1641c			NA	NA	NA	NA	NA	NA
1641c			NA	NA	NA	NA	NA	NA
	certified							
	value							
	range							
	percent		NA	NA	NA	NA	NA	NA
	difference							
			NA	NA	NA	NA	NA	NA
			NA	NA	NA	NA	NA	NA
			NA	NA	NA	NA	NA	NA
cass3 r1			0.926	0.0370	0.0343	0.107	0.0103	0.0160
cass3 r2			0.806	0.0230U	0.0330	0.119	0.0107	0.00999
cass3 r3			0.813	0.0230U	0.0331	0.119	0.0114	0.0103
cass3 rerun			0.929	0.0675	0.0321	0.123	0.0113	0.0145
	certified		1.09	0.042R	0.030	NC	NC	0.0120
	value							
	range		±0.07		±0.005			±0.004
	percent		15%	12%	14%	NA	NA	34%
	difference							
			26%	NA	10%	NA	NA	17%
			25%	NA	10%	NA	NA	14%
			15%	61%	7%	NA	NA	21%
Mean reagent blank (used to correct CASS)			0.0027	0.00289	0.00548	0.0111	0.00013	0.00425

Conventional Water Properties

The temperature, pH, salinity, and total suspended solids (TSS), referred to in this study as conventional water properties, were determined at the same stations where water was sampled for metals (Tables 1–3). The concentrations of these parameters were relatively uniform within each region, indicating the water was well mixed. The differences between the three regions were relatively small; the major exception was the lower salinity at Cherry Point due to the influence from the Fraser River. The temperature, pH, and salinity are similar to those reported by the WDOE (1997) Washington State Marine Water Quality Program for July 1994 and 1995 data collected at stations nearest the three regions sampled in this study.

The TSS concentrations generally ranged from 1 to 2 µg/L, which is typical for Puget Sound surface water during the summer. The concentration of phytoplankton appeared to be patchy within each region based both on the color of the water and the color of the filters used to determine the TSS. The TSS concentrations in Commencement Bay were significantly higher than those at the other two regions because of the turbidity from the Puyallup River, which was at high flow due to the late snow melt. The highest TSS was at station CB-9 located near the mouth of the river. Even though all stations in Commencement Bay were colored by the river plume, the salinity and temperature were fairly uniform, indicating relatively little dilution of the seawater.

Concentrations of Metals

The concentrations of total recoverable and dissolved metals in 10 water samples from each of the 3 regions are shown in Tables 7–9. These results have been blank-corrected using the mean of six field equipment blanks. Concentrations below the detection limit are flagged with a “U,” and the detection limit is listed. The concentrations of silver, beryllium, and selenium were frequently below detection. The concentrations of dissolved chromium, mercury, lead, and zinc were occasionally below detection.

Table 7. Concentrations of total recoverable and dissolved metals in seawater.

MARCH POINT STATIONS									
METALS IN WATER									
Sample Date: June 30, 1997									
(concentration in µg/L - blank corrected)									
MSL Code	Station No.	Type	Ag GFAA	Hg CVAA	Ba 9 ICP-MS	Cr 52 ICP-MS	Ni 60 ICP-MS	Cu 63 ICP-MS	Zn 66 ICP-MS
1114WSPA*39	MP1	TOTAL	0.011	0.000550	0.00284	0.225	0.453	0.434	0.886
1114WSPA*40	MP1 DUP	TOTAL	0.014	0.000576	0.00338	0.261	0.518	0.512	0.829
1114WSPA*44	MP2	TOTAL	0.010 U	0.000470	0.000733	0.287	0.498	0.465	0.487
1114WSPA*45	MP3	TOTAL	0.010 U	0.000411	0.00381	0.280	0.450	0.398	0.443
1114WSPA*46	MP4	TOTAL	0.010 U	0.000545	0.00101	0.308	0.490	0.432	0.502
1114WSPA*47	MP5	TOTAL	0.010 U	0.000554	0.00278	0.289	0.490	0.429	0.612
1114WSPA*48	MP6	TOTAL	0.010 U	0.000561	0.00304	0.289	0.510	0.488	0.550
1114WSPA*49	MP7	TOTAL	0.010 U	0.000538	0.00226	0.250	0.470	0.441	0.538
1114WSPA*50	MP8	TOTAL	0.010 U	0.000550	0.00249	0.407	0.487	0.459	0.708
1114WSPA*51	MP9	TOTAL	0.010 U	0.000631	0.00119	0.321	0.479	0.466	0.509
1114WSPA*52	MP10	TOTAL	0.010 U	0.000676	0.000484	0.279	0.522	0.489	1.26
1114WSPA*53	MP1	DISS	0.010 U	0.000320	0.000341 U	0.179	0.390	1.00	1.27
1114WSPA*54	MP1 DUP	DISS	0.010 U	0.000211	0.000341 U	0.185	0.426	0.405	0.176
1114WSPA*58	MP2	DISS	0.010 U	0.000257	0.000341 U	0.145	0.405	0.375	3.04
1114WSPA*59	MP3	DISS	0.010 U	0.000205 U	0.00265	0.183	0.398	0.403	0.323 J
1114WSPA*60	MP4	DISS	0.010 U	0.000548	0.00161	0.165	0.351	0.341	0.535
1114WSPA*61	MP5	DISS	0.010 U	0.000240	0.00173	0.181	0.403	0.357	0.297 J
1114WSPA*62	MP6	DISS	0.010 U	0.000572	0.000833	0.169	0.417	0.393	0.196 J
1114WSPA*63	MP7	DISS	0.010 U	0.000579	0.000341 U	0.162	0.381	0.375	0.251 J
1114WSPA*64	MP8	DISS	0.010 U	0.000321	0.00291	0.182	0.399	0.352	0.252 J
1114WSPA*65	MP9	DISS	0.010 U	0.000241	0.000683	0.161	0.440	0.388	0.176 J
1114WSPA*66	MP10	DISS	0.010 U	0.000205 U	0.000341 U	0.171	0.410	0.382	0.277 J
BLANKS									
1114WSPA*43 EB	MP1	TOTAL	0.029	0.000081	0.00381	0.121	0.0525	0.063	0.737
1114WSPA*57 EB	MP1	DISS	0.020	0.000089	0.000000	0.0885	0.0862	0.085	0.633
1114WSPA*197 TRP BLK			0.017	0.000210	0.00261	0.0977	0.0209	0.0838	0.631
Reagent Blank			0.007	0.000065	0.00164	0.0880	0.0241	0.0475	0.703
Mean Blank (used for blank correction):			0.018	0.000079	0.00063	0.0624	0.0401	0.0485	0.664
DETECTION LIMIT			0.010	0.0002	0.0003	0.063	0.080	0.12	0.34

Table 7. (Continued)

MARCH POINT STATIONS

METALS IN WATER

Sample Date: June 30, 1997

			(concentration in µg/L - blank corrected)					
MSL Code	Station No.	Type	As 75 ICP-MS	Se 77 ICP-MS	Cd 112 ICP-MS	Sb 121 ICP-MS	Tl 205 ICP-MS	Pb 207 ICP-MS
1114WSPA*39	MP1	TOTAL	0.743	0.0271	0.0591	0.0549	0.00911	0.0230
1114WSPA*40	MP1 DUP	TOTAL	0.984	0.0374	0.0864	0.0585	0.00896	0.0260
1114WSPA*44	MP2	TOTAL	1.01	0.0285	0.0611	0.0571	0.00903	0.0278
1114WSPA*45	MP3	TOTAL	1.15	0.0551	0.0672	0.0497	0.00901	0.0286
1114WSPA*46	MP4	TOTAL	1.09	0.0549	0.0662	0.0480	0.00928	0.0316
1114WSPA*47	MP5	TOTAL	1.10	0.0603	0.0656	0.0505	0.00907	0.0341
1114WSPA*48	MP6	TOTAL	0.987	0.0479	0.0611	0.0571	0.00868	0.0314
1114WSPA*49	MP7	TOTAL	1.05	0.0538	0.0652	0.0521	0.00849	0.0315
1114WSPA*50	MP8	TOTAL	1.04	0.0713	0.0558	0.0489	0.00891	0.0395
1114WSPA*51	MP9	TOTAL	0.982	0.0467	0.0543	0.0595	0.00854	0.0443
1114WSPA*52	MP10	TOTAL	1.01	0.0344	0.0594	0.0522	0.00941	0.0317
1114WSPA*53	MP1	DISS	0.963	0.0454	0.0555	0.0471	0.00805	0.0755
1114WSPA*54	MP1 DUP	DISS	0.982	0.0611	0.0573	0.0525	0.00810	0.00612 U
1114WSPA*58	MP2	DISS	1.04	0.0202 J	0.0612	0.0583	0.00919	0.00612 U
1114WSPA*59	MP3	DISS	1.18	0.110	0.0686	0.0505	0.00948	0.00612 U
1114WSPA*60	MP4	DISS	1.09	0.0533	0.0633	0.0560	0.00851	0.00612 U
1114WSPA*61	MP5	DISS	1.12	0.0563	0.0651	0.0584	0.00928	0.0118
1114WSPA*62	MP6	DISS	1.03	0.0645	0.0605	0.0621	0.00858	0.00612 U
1114WSPA*63	MP7	DISS	1.09	0.0653	0.0643	0.0537	0.00842	0.00612 U
1114WSPA*64	MP8	DISS	1.11	0.0358	0.0685	0.0525	0.00912	0.00612 U
1114WSPA*65	MP9	DISS	0.982	0.0476	0.0553	0.0552	0.00808	0.00612 U
1114WSPA*66	MP10	DISS	1.01	0.0506	0.0579	0.0494	0.00824	0.00612 U
BLANKS								
1114WSPA*43 EB	MP1	TOTAL	0.009	0.0151	0.00953	0.0268	0.000792	0.00632
1114WSPA*57 EB	MP1	DISS	0.003	0.0174	0.00989	0.0209	0.000943	0.00748
1114WSPA*197 TRP BLK			0.0018	0.0000	0.00849	0.0141	0.0000	0.00677
Reagent Blank			0.0064	0.0087	0.00758	0.0134	0.00024	0.00737
Mean Blank (used for blank correction):			0.00232	0.00541	0.00731	0.0151	0.000651	0.00641
DETECTION LIMIT			0.14	0.023	0.006	0.009	0.0006	0.006

Table 8. Concentrations of total recoverable and dissolved metals in seawater.

CHERRY POINT STATIONS
METALS IN WATER
Sample Date: July 16, 1997

(concentration in µg/L - blank corrected)									
MSL Code	Station ID	Type	Ag	Hg	Be 9	Cr 52	Ni 60	Cu 63	Zn 66
			GFAA	CVAA	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
1114WSPA*168	CP1	TOTAL	0.010 U	0.000485	0.000769	0.212	0.436	0.672	1.40
1114WSPA*169	CP1 Dup	TOTAL	0.010 U	0.000512	0.000341 U	0.217	0.459	0.701	1.89
1114WSPA*173	CP2	TOTAL	0.010 U	0.000430	0.000341 U	0.168	0.385	0.583	1.07
1114WSPA*174	CP3	TOTAL	0.010 U	0.000455	0.000341 U	0.111	0.400	0.636	1.13
1114WSPA*175	CP4	TOTAL	0.010 U	0.000458	0.000341 U	0.104	0.414	0.628	1.09
1114WSPA*176	CP5	TOTAL	0.010 U	0.000580	0.000341 U	0.115	0.439	0.657	0.948
1114WSPA*177	CP6	TOTAL	0.010 U	0.000561	0.000341 U	0.130	0.440	0.674	1.15
1114WSPA*178	CP7	TOTAL	0.010 U	0.000382	0.000341 U	0.146	0.402	0.625	0.983
1114WSPA*179	CP8	TOTAL	0.010 U	0.000487	0.000341 U	0.135	0.340	0.510	0.821
1114WSPA*180	CP9	TOTAL	0.010 U	0.000449	0.000341 U	0.153	0.384	0.591	1.20
1114WSPA*181	CP10	TOTAL	0.010 U	0.000563	0.000341 U	0.0878	0.411	0.601	0.880
1114WSPA*182	CP1	DISS	0.010 U	0.000395	0.000341 U	0.0627 U	0.341	0.498	0.637
1114WSPA*183	CP1 Dup	DISS	0.010 U	0.000283	0.000341 U	0.0933	0.374	0.530	0.793
1114WSPA*187	CP2	DISS	0.014	0.000235	0.000341 U	0.0846	0.384	0.580	1.08
1114WSPA*188	CP3	DISS	0.010 U	0.000301	0.000341 U	0.134	0.361	0.553	0.667
1114WSPA*189	CP4	DISS	0.010 U	0.000390	0.000341 U	0.0680	0.365	0.562	0.906
1114WSPA*190	CP5	DISS	0.010 U	0.000380	0.000341 U	0.0941	0.337	0.582	0.730
1114WSPA*191	CP6	DISS	0.010 U	0.000239	0.000341 U	0.0627 U	0.383	0.591	0.832
1114WSPA*192	CP7	DISS	0.010 U	0.000270	0.000341 U	0.0627 U	0.368	0.560	0.672
1114WSPA*193	CP8	DISS	0.010 U	0.000235	0.000341 U	0.0938	0.323	0.479	0.708
1114WSPA*194	CP9	DISS	0.010 U	0.000288	0.000341 U	0.0938	0.324	0.518	0.895
1114WSPA*195	CP10	DISS	0.010 U	0.000374	0.000341 U	0.113	0.392	0.560	0.763
BLANKS									
1114WSPA*172	CP1	TOTAL	0.011	0.000100	0.000000	0.000	0.0000	0.000	0.10
1114WSPA*186	CP1	DISS	0.021	0.000028	0.000000	0.0390	0.0507	0.049	1.36
1114WSPA*197 TRP BLK			0.011	0.000054	0.000000	0.0752	0.0181	0.0346	1.07
Reagent Blank			0.008	0.000037	0.000000	0.0000	0.0000	0.0000	0.0355
Mean Blank (used for blank correction):									
			0.018	0.000079	0.000063	0.0624	0.0401	0.0465	0.664
DETECTION LIMIT									
			0.010	0.000205	0.00034085	0.0627	0.0303	0.122	0.336

Table 8. (Continued)

CHERRY POINT STATIONS								
METALS IN WATER								
Sample Date: July 16, 1997								
(concentration in µg/L - blank corrected)								
MSL Code	Station ID	Type	As 75 ICP-MS	Se 77 ICP-MS	Cd 112 ICP-MS	Sb 121 ICP-MS	Tl 205 ICP-MS	Pb 207 ICP-MS
1114WSPA*168	CP1	TOTAL	0.590	0.0485	0.0446	0.0461	0.00735	0.0154
1114WSPA*169	CP1 Dup	TOTAL	0.539	0.0717	0.0481	0.0436	0.00758	0.0176
1114WSPA*173	CP2	TOTAL	0.432	0.0230 U	0.0439	0.0440	0.00770	0.0141
1114WSPA*174	CP3	TOTAL	0.411	0.0238	0.0447	0.0432	0.00790	0.0129
1114WSPA*175	CP4	TOTAL	0.450	0.0230 U	0.0480	0.0442	0.00739	0.0164
1114WSPA*176	CP5	TOTAL	0.489	0.0272	0.0480	0.0443	0.00793	0.0161
1114WSPA*177	CP6	TOTAL	0.433	0.0230 U	0.0441	0.0397	0.00683	0.0176
1114WSPA*178	CP7	TOTAL	0.447	0.0230 U	0.0461	0.0403	0.00698	0.0137
1114WSPA*179	CP8	TOTAL	0.465	0.0230 U	0.0403	0.0347	0.00653	0.0109
1114WSPA*180	CP9	TOTAL	0.459	0.0403	0.0473	0.0482	0.00749	0.0197
1114WSPA*181	CP10	TOTAL	0.505	0.0230 U	0.0487	0.0466	0.00733	0.0147
1114WSPA*182	CP1	DISS	0.493	0.0230 U	0.0330	0.0474	0.00724	0.00612 U
1114WSPA*183	CP1 Dup	DISS	0.466	0.0230 U	0.0318	0.0513	0.00738	0.00612 U
1114WSPA*187	CP2	DISS	0.414	0.0298	0.0312	0.0502	0.00745	0.00612 U
1114WSPA*188	CP3	DISS	0.577	0.0308	0.0368	0.0427	0.00744	0.0290
1114WSPA*189	CP4	DISS	0.445	0.0230 U	0.0390	0.0522	0.00755	0.00612 U
1114WSPA*190	CP5	DISS	0.421	0.0230 U	0.0414	0.0487	0.00775	0.00612 U
1114WSPA*191	CP6	DISS	0.415	0.0230 U	0.0370	0.0488	0.00758	0.00612 U
1114WSPA*192	CP7	DISS	0.439	0.0230 U	0.0357	0.0479	0.00736	0.00612 U
1114WSPA*193	CP8	DISS	0.541	0.0230 U	0.0398	0.0454	0.00781	0.00612 U
1114WSPA*194	CP9	DISS	0.416	0.0230 U	0.0394	0.0454	0.00792	0.00612 U
1114WSPA*195	CP10	DISS	0.470	0.0230 U	0.0395	0.0433	0.00746	0.00612 U
BLANKS								
1114WSPA*172	CP1	TOTAL	0.000	0.0000	0.00103	0.0014	0.00000	0.00008
1114WSPA*186	CP1	DISS	0.000	0.0000	0.0106	0.0141	0.000724	0.00722
1114WSPA*197 TRP BLK			0.0037	0.0000	0.00691	0.0121	0.000037	0.00455
Reagent Blank			0.0000	0.0000	0.00080	0.0013	0.00000	0.00000
Mean Blank (used for blank correction):			0.00232	0.00541	0.00731	0.0151	0.000651	0.00641
DETECTION LIMIT			0.140	0.0230	0.00594	0.00881	0.000583	0.00612

Table 9. Concentrations of total recoverable and dissolved metals in seawater.

COMMENCEMENT BAY STATIONS CONVENTIONAL WATER PROPERTIES Sample Date July 11, 1987									
(concentration in µg/L - blank corrected)									
MSL Code	Station No.	Type	Ag GFAA	Hg CVAA	Be 9 ICP-MS	Cr 52 ICP-MS	Ni 60 ICP-MS	Cu 63 ICP-MS	Zn 66 ICP-MS
1114WSPA*104	CB1	TOTAL	0.010 U	0.000711	0.000957	0.232	0.480	1.02	2.35
1114WSPA*105	CB1 DUP	TOTAL	0.010 U	0.000634	0.00175	0.279	0.442	0.98	2.16
1114WSPA*109	CB2	TOTAL	0.010 U	0.000909	0.00212	0.202	0.436	1.28	3.74
1114WSPA*110	CB3	TOTAL	0.029	0.000755	0.00168	0.220	0.466	0.782	1.30
1114WSPA*111	CB4	TOTAL	0.010 U	0.000342	0.00270	0.164	0.388	0.627	0.896
1114WSPA*112	CB5	TOTAL	0.010 U	0.000941	0.000341 U	0.200	0.454	1.25	4.36
1114WSPA*113	CB6	TOTAL	0.010 U	0.000833	0.00300	0.250	0.464	1.06	1.88
1114WSPA*114	CB7	TOTAL	0.010 U	0.000326	0.00218	0.171	0.395	0.620	1.09
1114WSPA*115	CB8	TOTAL	0.010 U	0.000820	0.000341 U	0.148	0.409	0.693	0.994
1114WSPA*116	CB9	TOTAL	0.010 U	0.000862	0.00408	0.370	0.548	1.02	1.21
1114WSPA*117	CB10	TOTAL	0.010 U	0.000550	0.000473	0.163	0.388	0.790	1.00
1114WSPA*118	CB1	DISS	0.010 U	0.000284	0.000341 U	0.128	0.381	0.577	1.85
1114WSPA*119	CB1 DUP	DISS	0.010 U	0.000219	0.000592	0.129	0.351	0.584	1.57
1114WSPA*123	CB2	DISS	0.010 U	0.000286	0.000341 U	0.0828	0.373	0.916	2.99
1114WSPA*124	CB3	DISS	0.010 U	0.000205 U	0.00117	0.128	0.335	0.505	0.783
1114WSPA*125	CB4	DISS	0.010 U	0.000208	0.000341 U	0.0979	0.348	0.467	0.657
1114WSPA*126	CB5	DISS	0.010 U	0.000497	0.000341 U	0.0994	0.496	1.09	4.31
1114WSPA*127	CB6	DISS	0.010 U	0.000208	0.000341 U	0.0722	0.353	0.697	1.33
1114WSPA*128	CB7	DISS	0.010 U	0.000205 U	0.000341 U	0.0928	0.333	0.491	0.735
1114WSPA*129	CB8	DISS	0.010 U	0.000233	0.000341 U	0.0781	0.276	0.439	0.572
1114WSPA*130	CB9	DISS	0.010 U	0.000205 U	0.000341 U	0.160	0.343	0.437	0.528
1114WSPA*131	CB10	DISS	0.010 U	0.000422	0.000341 U	0.140	0.337	0.531	0.844
BLANKS									
1114WSPA*108 EB	CB1	TOTAL	0.011	0.00112	0.000341 U	0.0827 U	0.0803 U	0.122 U	0.475
1114WSPA*122 EB	CB1	DISS	0.014	0.000205 U	0.000341 U	0.0872	0.0803 U	0.122 U	0.680
1114WSPA*197 TRP BLK			0.011	0.000205 U	0.000341 U	0.0868	0.0803 U	0.122 U	0.624
Reagent Blank			0.014	0.000087	0.00000	0.0390	0.0151	0.0376	0.651
Mean Blank (used for blank correction):			0.018	0.000079	0.00063	0.0824	0.0401	0.0465	0.654
DETECTION LIMIT			0.010	0.0002	0.0003	0.063	0.080	0.12	0.34

Table 9. (Continued)

COMMENCEMENT BAY STATIONS								
CONVENTIONAL WATER PROPERTIES								
Sample Date July 11, 1997								
(concentration in µg/L - blank corrected)								
MSL Code	Station No.	Type	As 75 ICP-MS	Se 77 ICP-MS	Cd 112 ICP-MS	Sb 121 ICP-MS	Tl 205 ICP-MS	Pb 207 ICP-MS
1114WSPA*104	CB1	TOTAL	1.03	0.0505	0.0574	0.0647	0.00932	0.0663
1114WSPA*105	CB1 DUP	TOTAL	1.03	0.0564	0.0607	0.0735	0.00837	0.0580
1114WSPA*109	CB2	TOTAL	1.00	0.0230 U	0.0572	0.0703	0.0103	0.141
1114WSPA*110	CB3	TOTAL	1.02	0.0404	0.0628	0.0785	0.00983	0.0657
1114WSPA*111	CB4	TOTAL	0.990	0.0303	0.0625	0.0803	0.00866	0.0453
1114WSPA*112	CB5	TOTAL	1.13	0.0294	0.0524	0.0769	0.00820	0.252
1114WSPA*113	CB6	TOTAL	1.00	0.0367	0.0591	0.0764	0.00889	0.143
1114WSPA*114	CB7	TOTAL	0.990	0.0398	0.0637	0.0745	0.00854	0.0479
1114WSPA*115	CB8	TOTAL	0.978	0.0256	0.0611	0.0808	0.00975	0.0563
1114WSPA*116	CB9	TOTAL	1.03	0.0643	0.0633	0.0706	0.0115	0.102
1114WSPA*117	CB10	TOTAL	0.985	0.0452	0.0629	0.0812	0.00919	0.0680
1114WSPA*118	CB1	DISS	0.971	0.0274	0.0582	0.0851	0.00893	0.00809
1114WSPA*119	CB1 DUP	DISS	0.943	0.0448	0.0575	0.0869	0.00897	0.00857
1114WSPA*123	CB2	DISS	0.925	0.0692	0.0538	0.0823	0.00948	0.0154
1114WSPA*124	CB3	DISS	0.902	0.0425	0.0588	0.0809	0.00923	0.00809
1114WSPA*125	CB4	DISS	0.931	0.0328	0.0609	0.0801	0.00977	0.00849
1114WSPA*126	CB5	DISS	0.991	0.0230 U	0.0531	0.0751	0.00819	0.0250
1114WSPA*127	CB6	DISS	0.909	0.0299	0.0548	0.0897	0.00823	0.0130
1114WSPA*128	CB7	DISS	0.920	0.0312	0.0597	0.0774	0.00953	0.00978
1114WSPA*129	CB8	DISS	0.797	0.105	0.0485	0.0632	0.00756	0.00969
1114WSPA*130	CB9	DISS	0.920	0.0435	0.0616	0.0726	0.00953	0.0151
1114WSPA*131	CB10	DISS	0.914	0.0230 U	0.0590	0.0738	0.00893	0.0120
BLANKS								
1114WSPA*108 EB	CB1	TOTAL	0.140 U	0.0230 U	0.00594 U	0.0125	0.000833	0.00612 U
1114WSPA*122 EB	CB1	DISS	0.140 U	0.0230 U	0.00843	0.0152	0.000618	0.0137
1114WSPA*197 TRP BLK			0.140 U	0.0230 U	0.00793	0.0144	0.000588 U	0.00612 U
Reagent Blank			0.0016	0.0000	0.00798	0.0187	0.00015	0.00537
Mean Blank (used for blank correction):			0.00232	0.00541	0.00731	0.0151	0.000651	0.00641
DETECTION LIMIT			0.14	0.023	0.006	0.009	0.0006	0.006

Discussion

Statistical Methods

Descriptive statistics were used to evaluate the distribution of blank-corrected concentration of each total and dissolved metal from water samples collected from the three Puget Sound regions. Analytical replicates for a given concentration were averaged prior to analysis. The distribution of each metal concentration within a region was characterized by the mean, median, minimum and maximum values, and the 25th and 75th quartiles. The range between the two quartiles provides a useful nonparametric interval bounding the distribution. The nonparametric median and first and third quartiles are not as greatly affected by single large observations, which can skew a mean and parametric confidence intervals. Possible outliers were defined as observations greater than three times the median value.

The mean concentrations of each total and dissolved metal from the three regions were compared using Tukey's Honestly Significant Difference (HSD) test. The HSD test compared all possible pairwise comparisons between regions using an experiment-wide error rate of $\alpha = 0.05$. Metal concentrations were transformed to the natural logarithm to minimize the heterogeneity of within-class variance. The Kruskal-Wallis nonparametric test of the equality of the three medians was used when the assumption of equal within-class variance was still not satisfied following the natural logarithmic transformation.

Particulate concentrations of each metal for each region were estimated by the difference in the median total and dissolved concentrations. The difference between median values was used rather than the difference between individual observations of the total and dissolved concentrations in an attempt to provide a more representative estimate of the particulate concentration in a region. If the median dissolved concentration was greater than the median total concentration, then the particulate concentration was not calculable.

Statistical Results

Three observations from Station MP1 at March Point were not used in the statistical analysis, because they were greater than two times the replicate result. These observations were for dissolved copper, zinc, and lead. The dissolved concentrations of these metals at this region were estimated only from the replicate with the lower concentration.

The distribution of the total concentration of each metal for each region is characterized in Table 10. The standard deviations for the majority of metals were generally less than 5%. Five observations had extreme values in relation to the median and could be considered outliers. Stations MP1 and CB3 had extreme values of total silver. Station MP8 had an extreme value of chromium, and Stations MP1 and CP1 had extreme values of zinc and selenium, respectively. Because there is no apparent reason for these high values, the data were not removed from further analysis.

The distribution of the concentration of dissolved metals is characterized in Table 11. The standard deviations for the majority of metals were again generally less than 5%. Ten observations had extreme values in relation to the median and could be considered outliers. Stations CP2 and CB2 had extreme values of total silver and beryllium, respectively. Station MP4 had an extreme low value of nickel, whereas Station CB5 had an extreme high value. Station MP2 had an extreme high value of zinc, and Station CB8 had an extreme low value of selenium. Stations CP3 and CB8 had extreme values of cadmium, and stations MP5 and CP3 had extreme values of lead. Again, because there is no apparent reason for these high and low values, the data were not removed from further analysis.

Concentrations of total and dissolved beryllium, chromium, nickel, arsenic, selenium, and cadmium were statistically greater ($\alpha = 0.05$) at March Point than Commencement Bay and Cherry Point (Table 12). Concentrations of copper, antimony, and thallium were statistically greater in Commencement Bay than at March Point and Cherry Point. Cherry Point tended to have the lowest concentrations of both the total and dissolved metals except for copper and zinc. Note that when stations are not listed in the

columns for statistical comparisons in Table 12, the missing values were not significantly different from those of either of the listed stations.

Variability Within Regions

Based on one sampling event, two regions, Cherry Point and March Point, apparently are not affected by local contamination. Commencement Bay is the only region that appears to have significant within-region differences for metals in water, with significantly higher concentrations of mercury, copper, zinc, and lead than the other regions, presumably due to industrial activity. The concentrations of these four metals are higher at stations CB2 and CB5 than at the other eight stations. The temperatures were the highest and the salinity the lowest at CB2 and CB5, indicating that these stations, located outside the Hylebos Waterway, are affected by the waterway. During the time of sampling, the tide was ebbing and the surface current was to the northwest, which is consistent with the assumption that the water chemistry at stations CB2 and CB5 is influenced by local sources in the northeastern area of the region.

Comparison to Previously Published Results on the Concentrations of Metals in Puget Sound

Over the past 20 years, there have been several studies in Puget Sound waters that used analytical methods sensitive enough to detect many of the metals discussed in the present study. The Pacific Marine Environmental Laboratory (PMEL) of NOAA published several articles on the distribution, sources, and transport of metals in Puget Sound, including Commencement Bay (NOAA 1987; Paulson and Feely 1985). The WDOE also has studied metals in Commencement Bay (Stinson and Norton 1987). The Municipality of Metropolitan Seattle (METRO) study on toxicant pretreatment measured 13 metals in the central Puget Sound and in the Strait of Juan de Fuca (Romberg et al. 1984). Other studies reported results for silver, arsenic, and mercury (Bloom and Crecelius 1983; Bloom and Crecelius 1984; Carpenter et al. 1978; and Crecelius et al. 1975). In general, the results of all these past studies are similar to the results in the present study. The metals that appear to be enriched in urban regions are chromium, copper, mercury, nickel, lead, and zinc. Several metals that were not significantly enriched by anthropogenic activities included arsenic, cadmium, antimony, and selenium. Several metals (silver, beryllium, and thallium) have not been studied adequately to determine geographical trends.

Table 10. Descriptive statistics of the total concentration ($\mu\text{g/L}$, blank corrected) of each metal for each region ($n = 10$).

Metal	Region	Mean	Median	St. Dev	Min	Max	Q1	Q3
Ag	March Point	0.0103	0.0100	0.00079	0.0100	0.0125	0.0100	0.0100U
	Cherry Point	0.0100	0.0100	0.00000	0.0100	0.0100	0.0100	0.0100U
	Commencement Bay	0.0119	0.0100	0.00601	0.0100	0.0290	0.0100	0.0100U
Hg	March Point	0.000560	0.000560	0.00008	0.000410	0.000680	0.000520	0.000640
	Cherry Point	0.000490	0.000470	0.00006	0.000380	0.000570	0.000440	0.000560
	Commencement Bay	0.000700	0.000790	0.00022	0.000330	0.000940	0.000500	0.000870
Be	March Point	0.00272	0.00300	0.00115	0.00111	0.00444	0.00157	0.00369
	Cherry Point	0.000530	0.000340	0.00029	0.000340	0.00118	0.000340	0.000710
	Commencement Bay	0.00244	0.00252	0.00126	0.000860	0.00471	0.00107	0.00341
Cr	March Point	0.291	0.284	0.04560	0.239	0.403	0.268	0.307
	Cherry Point	0.132	0.129	0.03660	0.0837	0.210	0.105	0.153
	Commencement Bay	0.210	0.197	0.06580	0.144	0.365	0.159	0.247

Table 10. (Continued)

Ni	March Point	0.530	0.530	0.02146	0.490	0.562	0.517	0.544
	Cherry Point	0.446	0.447	0.03230	0.381	0.488	0.425	0.480
	Commencement Bay	0.481	0.485	0.04950	0.427	0.588	0.433	0.505
Cu	March Point	0.500	0.508	0.02877	0.444	0.535	0.478	0.523
	Cherry Point	0.666	0.673	0.05140	0.556	0.733	0.635	0.708
	Commencement Bay	0.955	0.939	0.25000	0.666	1.33	0.723	1.17
Zn	March Point	0.4466	0.336	0.21830	0.336	1.01	0.336	0.498
	Cherry Point	0.8456	0.832	0.19420	0.574	1.30	0.727	0.917
	Commencement Bay	1.625	1.011	1.23300	0.649	4.11	0.752	2.38
As	March Point	1.03	1.03	0.08100	0.856	1.16	0.988	1.09
	Cherry Point	0.468	0.457	0.04440	0.413	0.567	0.435	0.496
	Commencement Bay	1.02	1.00	0.04340	0.980	1.13	0.991	1.03
Se	March Point	0.0539	0.0563	0.01350	0.0340	0.0768	0.0393	0.0618
	Cherry Point	0.0314	0.0244	0.01395	0.0230	0.0655	0.0230	0.0359
	Commencement Bay	0.0437	0.0437	0.01372	0.0230	0.0697	0.0338	0.0526
Cd	March Point	0.0703	0.0713	0.00410	0.0616	0.0746	0.0680	0.0736
	Cherry Point	0.0451	0.0455	0.00255	0.0396	0.0480	0.0434	0.0473
	Commencement Bay	0.0597	0.0611	0.00355	0.0518	0.0630	0.0579	0.0623
Sb	March Point	0.0682	0.0673	0.00398	0.0631	0.0746	0.0646	0.0722
	Cherry Point	0.0399	0.0410	0.00388	0.0316	0.0451	0.0371	0.0422
	Commencement Bay	0.0728	0.0736	0.00456	0.0660	0.0781	0.0675	0.0773
Tl	March Point	0.00960	0.00967	0.00030	0.00914	0.0101	0.00930	0.00977
	Cherry Point	0.00788	0.00798	0.00035	0.00718	0.00835	0.00759	0.00812
	Commencement Bay	0.0102	0.0103	0.00093	0.00885	0.0122	0.00949	0.0106
Pb	March Point	0.0389	0.0380	0.00573	0.0309	0.0507	0.0348	0.0419
	Cherry Point	0.0144	0.0146	0.00252	0.0101	0.0189	0.0127	0.0159
	Commencement Bay	0.0975	0.0660	0.06480	0.0444	0.251	0.0534	0.141

Table 11. Descriptive statistics for the dissolved concentration ($\mu\text{g/L}$, blank corrected) of each metal for each region ($n = 10$).

Metal	Region	Mean	Median	St. Dev.	Min	Max	Q1	Q3
Ag	March Point	0.0100	0.0100	0.00000	0.0100	0.0100	0.0100	0.0100
	Cherry Point	0.0104	0.0100	0.00126	0.0100	0.0140	0.0100	0.0100
	Commencement Bay	0.0100	0.0100	0.00000	0.0100	0.0100	0.0100	0.0100
Hg	March Point	0.000340	0.000260	0.00016	0.000210	0.000580	0.000230	0.000550
	Cherry Point	0.000300	0.000290	0.00006	0.000230	0.000390	0.000240	0.000360
	Commencement Bay	0.000270	0.000220	0.00010	0.000210	0.000500	0.000210	0.000320
Be	March Point	0.00166	0.00149	0.00117	0.000150	0.00354	0.000570	0.00259
	Cherry Point	0.000340	0.000340	0.00000	0.000340	0.000340	0.000340	0.000340
	Commencement Bay	0.000580	0.000340	0.00047	0.000340	0.00180	0.000340	0.000640
Cr	March Point	0.165	0.166	0.01165	0.141	0.179	0.157	0.177
	Cherry Point	0.0826	0.0779	0.02258	0.0627	0.129	0.0627	0.0945
	Commencement Bay	0.104	0.0945	0.02952	0.0680	0.156	0.0774	0.127
Ni	March Point	0.441	0.444	0.02332	0.391	0.480	0.434	0.452
	Cherry Point	0.396	0.402	0.02128	0.363	0.432	0.374	0.406
	Commencement Bay	0.396	0.386	0.05630	0.316	0.538	0.374	0.408
Cu	March Point	0.425	0.425	0.02246	0.387	0.451	0.402	0.446
	Cherry Point	0.594	0.606	0.03410	0.525	0.637	0.563	0.613
	Commencement Bay	0.656	0.564	0.22020	0.484	1.14	0.506	0.753
Zn	March Point	0.581	0.336	0.77600	0.336	2.79	0.336	0.336
	Cherry Point	0.552	0.500	0.15030	0.336	0.836	0.452	0.666
	Commencement Bay	1.21	0.567	1.25200	0.336	4.07	0.391	1.78
As	March Point	1.06	1.06	0.06820	0.965	1.18	1.00	1.11
	Cherry Point	0.464	0.444	0.05660	0.417	0.579	0.418	0.497
	Commencement Bay	0.919	0.922	0.04950	0.799	0.993	0.909	0.940
Se	March Point	0.0611	0.0587	0.02330	0.0256	0.116	0.0501	0.0701
	Cherry Point	0.0255	0.0230	0.00535	0.0230	0.0362	0.0230	0.0260
	Commencement Bay	0.0482	0.0399	0.02627	0.0230	0.111	0.0327	0.0553
Cd	March Point	0.0694	0.0696	0.00469	0.0626	0.0759	0.0648	0.0732
	Cherry Point	0.0365	0.0373	0.00332	0.0306	0.0408	0.0342	0.0389
	Commencement Bay	0.0561	0.0576	0.00416	0.0478	0.0609	0.0529	0.0593

Table 11. (Continued)

Metal	Region	Mean	Median	St. Dev.	Min	Max	Q1	Q3
Sb	March Point	0.0685	0.0682	0.00305	0.0645	0.0735	0.0654	0.0711
	Cherry Point	0.0444	0.0452	0.00302	0.0396	0.0491	0.0418	0.0465
	Commencement Bay	0.0750	0.0757	0.00750	0.0601	0.0866	0.0704	0.0801
Tl	March Point	0.00935	0.00919	0.00053	0.00872	0.0101	0.00885	0.00986
	Cherry Point	0.00815	0.00810	0.00017	0.00796	0.00846	0.00800	0.00828
	Commencement Bay	0.00959	0.00974	0.00072	0.00821	0.0104	0.00887	0.0102
Pb	March Point	0.00955	0.00877	0.00325	0.00607	0.0182	0.00810	0.00977
	Cherry Point	0.00832	0.00612	0.00696	0.00612	0.0281	0.00612	0.00612
	Commencement Bay	0.0117	0.0101	0.00515	0.00727	0.0242	0.00763	0.0143

Table 12. Statistical comparisons and ranking of regions for the total and dissolved concentrations and estimated particulate concentrations of each metal ($\mu\text{g/L}$, blank corrected). Significantly greater concentrations are designated by a "greater than" sign (>), and concentrations not significantly different are separated by a comma.

Metal	Region	Total		Dissolved		Estimated Particulate Concentration
		Median	Statistical Comparison	Median	Statistical Comparison	
Ag	March Point	0.0100	NS	0.0100	NS	0.0000
	Cherry Point	0.0100		0.0100		0.0000
	Commencement Bay	0.0100		0.0100		0.0000
Hg	March Point	0.000560	CB>CP	0.000260	NS	0.000300
	Cherry Point	0.000470		0.000290		0.000180
	Commencement Bay	0.000790		0.000220		0.000570
Be	March Point	0.00300	MP,CB>CP	0.00149	MP>CB,CP	0.00151
	Cherry Point	0.000340		0.000340		0.00000
	Commencement Bay	0.00252		0.000340		0.00218
Cr	March Point	0.284	MP>CB>CP	0.166	MP>CB,CP	0.118
	Cherry Point	0.129		0.0779		0.0506
	Commencement Bay	0.197		0.0945		0.102
Ni	March Point	0.530	MP>CB,CP	0.444	MP>CB,CP	0.0863
	Cherry Point	0.447		0.402		0.0448
	Commencement Bay	0.485		0.386		0.0995
Cu	March Point	0.508	CB>CP>MP	0.425	CB,CP>MP	0.0835
	Cherry Point	0.673		0.606		0.0665
	Commencement Bay	0.939		0.564		0.375
Zn	March Point	0.336	CB,CP>MP	0.336	NS	0.000
	Cherry Point	0.832		0.500		0.333
	Commencement Bay	1.011		0.567		0.444

Table 12. (Continued)

Metal	Region	Total		Dissolved		Estimated Particulate Concentration
		Median	Statistical Comparison	Median	Statistical Comparison	
As	March Point	1.03	MP,CB>CP	1.06	MP>CB>CP	NA
	Cherry Point	0.457		0.444		0.0124
	Commencement Bay	1.00		0.922		0.0801
Se	March Point	0.0563	MP>CP	0.0587	MP,CB>CP	NA
	Cherry Point	0.0244		0.0230		0.00144
	Commencement Bay	0.0437		0.0399		0.00379
Cd	March Point	0.0713	MP>CB>CP	0.0696	MP>CB>CP	0.00175
	Cherry Point	0.0455		0.0373		0.00823
	Commencement Bay	0.0611		0.0576		0.00350
Sb	March Point	0.0673	CB,MP>CP	0.0682	CB>MP>CP	NA
	Cherry Point	0.0410		0.0452		NA
	Commencement Bay	0.0736		0.0757		NA
Tl	March Point	0.00967	CB,MP>CP	0.00919	CB,MP>CP	0.000480
	Cherry Point	0.00798		0.00810		NA
	Commencement Bay	0.0103		0.00974		0.000510
Pb	March Point	0.0380	CB>MP>CP	0.00877	NS	0.0292
	Cherry Point	0.0146		0.00612		0.00848
	Commencement Bay	0.0660		0.0101		0.0560
MP = March Point CP = Cherry Point CB = Commencement Bay NS = Not Significant NA = Not Applicable						

Conclusions

The concentrations of 13 metals were determined in three regions of Puget Sound during the summer of 1997. The seawater samples were collected and analyzed using EPA methods designed to minimize sample contamination and to determine the ambient concentrations of metals in uncontaminated coastal seawater. Results for field equipment blanks and reagent blanks indicate that very little contamination occurred from sampling and analysis. The detection limits obtained were well below those required by the WDOE. Several metals including silver, beryllium, lead, selenium, and zinc were near or below the detection limits in some samples. Both dissolved metals (filtered at 0.45 µm) and total recoverable metals were determined at 10 stations in surface water (1-m depth). Samples were collected near Cherry Point (northwest of Bellingham), March Point (near Anacortes), and Commencement Bay.

The concentrations of metals were very uniform within a region, except for Commencement Bay, where several stations indicate local industrial contamination of copper, mercury, lead, and zinc. These

results are consistent with results from other studies that were able to quantify metals at similar detection limits. There were relatively small differences between the mean concentrations of metals in the three regions. Cherry Point samples contained lower concentrations of arsenic, cadmium, antimony, selenium, and thallium, probably due to dilution of seawater by the Fraser River.

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